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(72) Inventors:
• **Dalle, Frederic**
06110 Le Canet (FR)
• **Marteaux, Leon**
1160 Bruxelles (BE)

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(71) Applicant: **DOW CORNING S.A.**
B-7180 Seneffe (BE)

(74) Representative: **Vandamme, Luc Johan Roger**
Dow Corning Limited
Cardiff Road
Barry South Glamorgan CF6 7YL Wales (GB)

(54) Method of making silicone oil-in-water emulsions

(57) A silicone oil-in-water emulsion containing a linear non-crosslinked silicone copolymer is prepared by polymerizing an OH endblocked polydiorganosiloxane with an amine functional trialkoxysilane in the presence of a metal catalyst. However, the polymerization is interrupted by the emulsification of this copolymer, and a

carboxylic anhydride is added prior to the emulsification. The resulting emulsions are particularly useful in most personal care applications, and they also have value in textile fibre treatment, leather lubrication, fabric softening, as release agents, in water based coatings, for oil drag reduction, lubrication, and for the facilitation of cutting of cellulose materials.

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Description

[0001] This invention is directed to a method of making an oil-in-water (O/W) emulsion wherein the oil component of the emulsion is a polymer containing a silicon atom. More particularly, the method involves polymerization of an OH endblocked polydiorganosiloxane, preferably polydimethylsiloxane with an amine functional trialkoxysilane in the presence of a metal catalyst, and an interruption of the polymerization reaction by an emulsification. The addition of an anhydride prior to the emulsification is done to avoid further cure reversion.

[0002] Commercial emulsions containing an amine functional polydimethylsiloxane fluid are limited in their market appeal as they are known to contain only relatively low viscosity amine functional polydimethylsiloxane fluids, that is amine functional polydimethylsiloxane fluids having a viscosity of at most, up to about 25,000 mm²/s at 25°C. However, there exists a need, especially in the personal care arena, for emulsions containing higher molecular weight, and correspondingly higher viscosity linear amine functional polydimethylsiloxane fluids.

[0003] In addition, these commercial emulsions may often contain about one percent of a volatile cyclic species of polydimethylsiloxane such as octamethylcyclotetrasiloxane in addition to the low viscosity amine functional polydimethylsiloxane fluid, and this content of volatile species is unacceptable according to some recent safety and environmental regulations and guidelines.

[0004] While higher viscosity polysiloxane polymers with a content of volatile cyclic species less than 0.5 percent have been obtained by reacting certain polysiloxanes with a crosslinking agent in the presence of a catalyst, such chain extensions have been obtained using an OH endblocked polydimethylsiloxane and a dialkoxysilane. This procedure is very slow and often takes weeks in order to reach completion. When such processes have been attempted to be modified in order to speed up the reaction, the use of a trialkoxysilane instead of a dialkoxysilane has led to the production of crosslinked elastomeric materials which are undesirable in many applications.

[0005] Where the prior art does refer to an emulsion containing an amine functional polydimethylsiloxane, the patents are either silent as regards the particular viscosity or molecular weight of the amine functional polydimethylsiloxane fluid contained in the emulsion, or where the viscosity or molecular weight of the amine functional polydimethylsiloxane fluid is mentioned, it is significantly below the levels now required in the personal care arena industry-wise. In patents where a higher viscosity or a higher molecular weight of the amine functional polydimethylsiloxane fluid is mentioned, however, the patents are generally silent as to how the emulsion is prepared. One example is US Patent 5,326,483.

[0006] Although the prior art known to applicants is replete with patents relating to various types of cured systems containing high viscosity and high molecular weight polysiloxanes, it is not known to employ a trialkoxysilane in order to polymerize an OH endblocked polydiorganosiloxane or polydimethylsiloxane in bulk, and to produce by such a procedure, a high molecular weight linear non-crosslinked silicone polymer in emulsion form. This is the essence of the contribution of the present invention.

[0007] Moreover, it is not known to conduct a polymerization, and then to interrupt the process of polymerization by addition of an anhydride and by emulsification, particularly in a silicone system based on OH endblocked polydimethylsiloxane or polydiorganosiloxane, which is known to be unstable and subject to reversion, i.e., depolymerization or post polymerization. However, by the addition of a low level of a carboxylic anhydride directly into the silicone polymer prior to its emulsification, applicants herein have discovered an efficient means avoid this type of reversion.

[0008] The present invention enables the manufacture of a silicone polymer utilizing a silicone cure system in which a trialkoxysilane is employed, and the interruption of the polymerization when a desired viscosity has been achieved by a step of anhydride addition and emulsification. While this process can be used to make emulsions containing a silicone polymer having a viscosity in the range of from about 1,000 mm²/sec to 1,000,000 mm²/sec, it is most preferred that the silicone polymer in the emulsion have a viscosity generally in the range of about 30,000 mm²/sec to about 500,000 mm²/sec.

[0009] Thus, according to the present invention, a linear silicone polymer can be obtained provided there is employed a low amount of trialkoxysilane, and provided the step of interrupting polymerization is carried out when the polymer is still linear. In essence, therefore, the emulsification is used in order to stop the polymerization. Reversion of the polymer is avoided by inclusion of an acid anhydride to the polymer prior to emulsification.

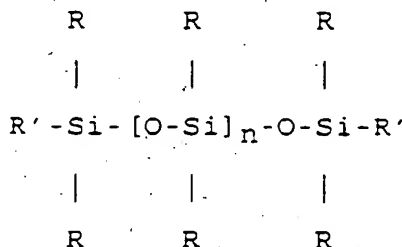
[0010] Among the benefits obtained according to the present invention there is included that a useful silicone emulsion can be provided, containing a much higher molecular weight linear amine functional polysiloxane polymer which possesses e.g. improved hair conditioning than can be presently obtained with state of the art manufacturing techniques.

[0011] In addition, the use of a trialkoxysilane significantly speeds up the polymerization kinetics when compared to techniques employing a dialkoxysilane, and quite unexpectedly, this does not lead to a crosslinked material when the trialkoxysilane is used in low amounts, and polymerization is stopped by anhydride addition and emulsification. While the trialkoxysilane can be used in an amount as high as about 5% by weight, it is preferred to use it at a level which is generally less than about 3% by weight.

[0012] The method according to the present invention is carried out in essentially two steps. The first step involves

polymerization of an OH endblocked polydiorganosiloxane, preferably polydimethyl siloxane with an amine functional trialkoxysilane, in the presence of a metal catalyst. In the second step, the condensation reaction occurring in the first step is interrupted by addition of an anhydride and by emulsification as a result of the addition of one or more surfactants and water.

[0013] The polydiorganosiloxane used in the above reaction in the first step of the process generally comprises a substantially linear polymer of the structure:



[0014] In this structure, each R independently represents a hydrocarbon group having up to 20 carbon atoms, such as an alkyl group, representative of which are methyl, ethyl, propyl, or butyl. R can also be an aryl group such as phenyl. R' represents -OH, n is a positive integer greater than one. Preferably n is an integer which results in the polymer being a polysiloxane with a viscosity between about 1 and about 1×10^6 mm²/sec at 25 °C.

[0015] If desired, the polydiorganosiloxane can have a small amount of branching, e.g. less than 2 mole% of the siloxane units, without affecting the invention, i.e., the polymers are substantially linear. Preferably, all of the R groups are methyl groups.

[0016] The organosilicon material which reacts with the OH endblocked polydiorganosiloxane in the condensation reaction is an amine functional trialkoxysilane. This material can be represented by the formula Q-Si-(OR^{*})₃ where R^{*} is an alkyl group containing 1-6 carbon atoms; Q denotes an amine functional substituent of the formula -R''Z wherein R'' is a divalent alkylene radical of 3 to 6 carbon atoms; and Z is a monovalent radical selected from the group consisting of -NR₂'', and -NR''(CH₂)_mNR₂'', where R'' denotes hydrogen or an alkyl group of 1 to 4 carbons, and m is a positive integer having a value of from 2 to 6.

[0017] Suitable R^{*} groups are represented by and may be independently selected from among methyl, ethyl, propyl, isopropyl, butyl, and isobutyl.

[0018] The alkylene radicals represented by R'' may include trimethylene, tetramethylene, pentamethylene, -CH₂CHCH₃CH₂-, and -CH₂CH₂CHCH₃CH₂-. Silanes where R'' is a trimethylene or an alkyl substituted trimethylene radical such as -CH₂CHCH₃CH₂-, are preferred.

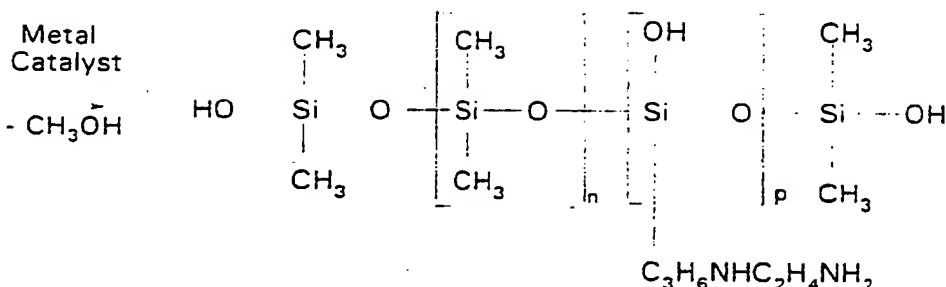
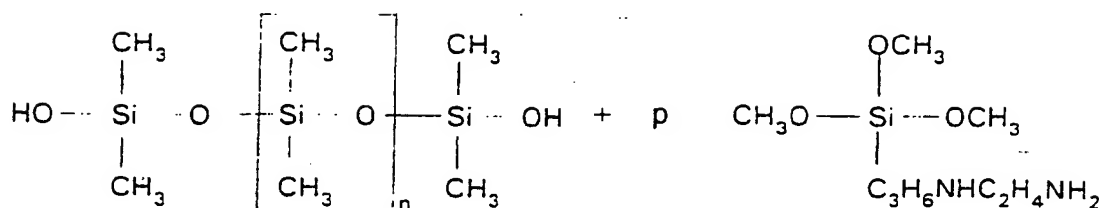
[0019] Useful Z radicals include the unsubstituted amine radical -NH₂, alkyl substituted amine radicals such as -NHCH₃, -NHCH₂CH₂CH₂CH₃, and -N(CH₂CH₃)₂; and aminoalkyl substituted amine radicals such as -NHCH₂CH₂NH₂, -NH(CH₂)₆NH₂, and -NHCH₂CH₂CH₂N(CH₃)₂.

[0020] Some representative commercially available amine functional trialkoxysilanes which can be used are 4-aminobutyltriethoxysilane; N-(2-aminoethyl)-3-aminopropyltrimethoxysilane; N-(6-aminoethyl)aminopropyltrimethoxysilane; 3-aminopropyltriethoxysilane; 3-aminopropyltrimethoxysilane; (3-aminopropyl)tris[2-(2-methoxyethoxy)ethoxy]silane; and 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane.

[0021] If desired, other types of functional trialkoxysilanes can also be used herein, such as epoxyfunctional trialkoxysilanes, acryloxyfunctional trialkoxysilanes, and methacryloxyfunctional trialkoxysilanes, for example. Some representative compositions which can be used include 3-(glycidoxypropyl)trimethoxysilane, [β-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane, 5,6-(epoxyhexyl)trimethoxysilane, 3-(acryloxypropyl)trimethoxysilane, and 3-(methacryloxypropyl)trimethoxysilane.

[0022] The metal catalyst for the reaction of the =Si-OH with the =Si-OR is preferably an organotin salt, some examples of which include stannous octoate, dimethyltin dilaurate, dibutyltin dilaurate, dibutyltin diacetate, dimethyltin dineodecanoate, dibutyltin dimethoxide, isobutyl tin triceroate, dimethyltin dibutyrate, triethyltin tartrate, tin oleate, tin naphthonate, tin butyrate, tin acetate, tin benzoate, tin sebacate, and tin succinate. Generally, the catalyst is used in amounts of between about 0.001 and 10 weight percent based on the weight of the OH endblocked polydiorganosiloxane.

[0023] The polymerization reaction occurring in the first step of the process, is a condensation reaction involving the OH endblocked polydiorganosiloxane, the aminotrialkoxysilane, and the metal catalyst, which can be illustrated by the specific example depicted as seen below:



[0024] The condensation reaction is slowed down by the addition of an acid anhydride, preferably a carboxylic anhydride, such as acetic anhydride (CH₃CO)₂O or benzoic anhydride (C₆H₅CO)₂O. Other carboxylic anhydrides can also be used, such as succinic anhydride, phthalic anhydride, and maleic anhydride.

[0025] Following this addition, the resulting linear OH endblocked amine functional siloxane copolymer is emulsified using water and a suitable surfactant or mixture of surfactants.

[0026] The surfactant can be a non-ionic surfactant, a cationic surfactant, an anionic surfactant, an alkylpolysaccharide, or an amphoteric surfactant. If desired, a silicone polyether can also be employed.

[0027] Examples of non-ionic surfactants include polyoxyalkylene alkyl ethers, polyoxyalkylene sorbitan alkyl esters, polyoxyalkylene alkyl esters, and polyoxyalkylene alkylphenol ethers, polyethylene glycols, polypropylene glycols, and diethylene glycols.

[0028] Examples of cationic surfactants include quaternary ammonium hydroxides such as tetramethylammonium hydroxide, cetyltrimethylammonium methosulfate, alkyltriethoxyethylammonium acetate, octyltrimethylammonium hydroxide, dodecyltrimethyl ammonium hydroxide, hexadecyltrimethyl ammonium hydroxide, octyldimethylbenzylammonium hydroxide, decyldimethylbenzyl ammonium hydroxide, didodecyldimethyl ammonium hydroxide, dioctadecyl dimethylammonium hydroxide, tallow trimethylammonium hydroxide and cocotrimethylammonium hydroxide, as well as corresponding salts of these materials; fatty acid amines and amides and their derivatives, and the salts of the fatty acid amines and amides, including aliphatic fatty amines and their derivatives, homologues of aromatic amines having fatty chains, fatty amides derived from aliphatic diamines, fatty amides derived from disubstituted amines, derivatives of ethylene diamine, amide derivatives of amino alcohols, amine salts of long chain fatty acids, quaternary ammonium bases derived from fatty amides of disubstituted diamines quaternary ammonium bases of benzimidazolines; basic compounds of pyridinium and its derivatives; sulfonium compounds; quaternary ammonium compounds of betaine; urethanes of ethylene diamine; polyethylene diamines; and polypropanol polyethanol amines.

[0029] Examples of suitable anionic surfactants include alkyl sulfates such as lauryl sulfate; polymers such as an acrylate/C₁₀₋₃₀ alkyl acrylate crosspolymer; alkylbenzenesulfonic acids and salts, such as hexylbenzenesulfonic acid, octylbenzenesulfonic acid, decylbenzenesulfonic acid, dodecylbenzenesulfonic acid, cetylbenzenesulfonic acid and myristylbenzenesulfonic acid; the sulfate esters of monoalkyl polyoxyethylene ethers; alkylnaphthylsulfonic acid; alkali metal sulfonates; sulfonated glyceryl esters of fatty acids, such as sulfonated monoglycerides of coconut oil acids, salts of sulfonated monovalent alcohol esters, amides of amino sulfonic acids, sulfonated products of fatty acid nitriles, sulfonated aromatic hydrocarbons, condensation products of naphthalene sulfonic acids with formaldehyde, sodium octahydroanthracene sulfonate; alkali metal alkyl sulfates; ester sulfates; and alkarylsulfonates.

[0030] Examples of some suitable alkylpolysaccharide surfactants include, for example, materials of the structure R¹-O-(R²O)_a-(G)_b wherein R¹ represents a linear or branched alkyl group, a linear or branched alkenyl group, or an alkylphenyl group; R² represents an alkylene group; G is a reduced sugar; a denotes 0 or a positive integer; and b represent a positive integer. These types of surfactants are described in detail, for example in US patent 5,035,832.

[0031] Examples of suitable amphoteric surfactants include cocamidopropyl betaine and cocamidopropyl hydroxysulfate.

[0032] The above surfactants may be used individually or in combination.

[0033] The particle size of the silicone in the emulsion is dependent on, among other factors, the amount and type of surfactant employed. The amount of surfactant used will vary depending on the surfactant, but generally, it is used in an amount of between about 1 and 30 weight percent based on the total weight of the OH endblocked polydimethylsiloxane. The particle size range starts at 0.2 μm , but it is preferably from about 0.3 μm to about 1.5 μm .

[0034] The final material used to form the emulsions herein is water, which forms the continuous phase of the emulsion, and into which the silicone oil droplets are dispersed.

[0035] If desired, other materials can be added to either phase of the emulsion. For example, perfumes, colorants, thickeners, preservatives, plasticizers, and active ingredients such as pharmaceuticals may be included.

[0036] It is preferred that the linear OH endblocked amine functional siloxane copolymer, the surfactant and water are mixed by simple agitation to form a coarse water in oil mixture. This mixture is then emulsified. During emulsification, the coarse water in oil mixture is inverted into a fine silicone in water emulsion. The emulsification can be accomplished by conventional means such as a batch mixer, colloid mill or line mixer. The emulsification process is, thus, simple and fast.

[0037] The linear OH endblocked amine functional siloxane copolymer, the surfactant, and water, can be mixed all at once or, alternatively, the materials can be mixed in any order, provided that water is the last component.

[0038] The emulsions of this invention are useful in most standard applications for silicone emulsions. Thus, they are useful for personal care applications, such as on hair, skin, mucous, and teeth. In these applications, the silicone is lubricious and will improve the properties of skin creams, skin care lotions, moisturizers, facial treatments such as acne or wrinkle removers, personal and facial cleansers, bath oils, perfumes, fragrances, colognes, sachets, sunscreens, pre-shave and after shave lotions, shaving soaps, and shaving lathers. It can likewise be used in hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories, and cuticle coats, to provide conditioning benefits. In cosmetics, it functions as a levelling and spreading agent for pigments, in make-ups, colour cosmetics, foundations, blushes, lipsticks, eye liners, mascaras, oil removers, colour cosmetic removers, and powders. It is likewise useful as a delivery system for oil and water soluble substances, such as vitamins, organic sunscreens, ceramides, and pharmaceuticals. When compounded into sticks, gels, lotions, aerosols, and roll-ons, the emulsions of this invention impart a dry silky-smooth payout.

[0039] When used in personal care products, the emulsions are generally incorporated in amounts of about 0.01 to about 50 weight percent, preferably 0.1 to 25 weight percent of the personal care product. They can be added to conventional ingredients for the personal care product selected. Thus, they can be mixed with deposition polymers, surfactants, detergents, antibacterials, antidandruffs, foam boosters, proteins, moisturising agents, suspending agents, opacifiers, perfumes, colouring agents, plant extracts, polymers, and other conventional personal care ingredients.

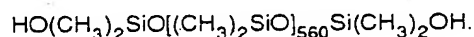
[0040] Beyond personal care, the emulsions of the invention are useful for other applications such as in textile fibre treatment, leather lubrication, fabric softening, release agents, water based coatings, oil drag reduction, lubrication, and facilitation of cutting cellulose materials.

[0041] Other variations may be made in compounds, compositions, and methods described herein without departing from the essential features of the invention.

[0042] The following examples are set forth for the purpose of illustrating the invention in more detail. All parts and percentages are given by weight, unless otherwise indicated, and viscosity is measured at 25°C.

Example 1

[0043] A cationic emulsion was prepared by mixing 49.64 gram of an OH endblocked polydimethylsiloxane having a degree of polymerization of about 560, 0.1 gram of a tin catalyst, and 0.26 gram of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane. The tin catalyst used in this example was dimethyltin dineodecanoate. By *degree of polymerization* is meant that the value of "n" in the formula shown above for the polydimethylsiloxane monomer was about 560. Thus, the polydimethylsiloxane monomer had a structure generally corresponding to the formula



An amine functional siloxane polymer with a viscosity of 100,000 mm^2/s was obtained within 35 minutes at 40 °C. It was still flowable and was capable of being mechanically emulsified. There was then conducted a phase inversion emulsification in order to stop further polymerization. This was accomplished by adding to the polymer 0.4 gram of acetic anhydride to avoid any reverse depolymerization. This was followed by the addition of 3 gram of Renex 30, 2 gram of Arquad 16-29, and 4 gram of water. Arquad 16-29, it is noted, is a cationic surfactant, and an N-alkyl trimeth-

ylammonium chloride. It is a product of Akzo Chemicals, Inc., Chicago, Illinois. Renex 30 is a nonionic surfactant with an HLB of 14.5. It is a polyoxyethylene ether alcohol, and a product of ICI Surfactants, Wilmington, Delaware.

[0044] The mixture was sheared sufficiently to accomplish the phase inversion, and shearing was continued until there had been obtained a reduction in the particle size to within a range of about 0.3-0.8 micrometer. To the sheared mixture was added 40.6 gram of dilution water.

[0045] A rheological study of the polymer prepared and emulsified in this example showed that no crosslinking had occurred. This was evidenced by the fact that the $\tan \delta$ or the loss factor, which is a ratio of the viscous modulus G'' to the elastic modulus G' , corresponded to $\tan \delta$ s for known linear amine functional siloxane polymers of a viscosity of 100,000 mm²/s, which typically have a value of about 10 at 1 hertz (Hz). It should be pointed out that $\tan \delta$ is a property generally relevant to, and used to characterize crosslinked materials, i.e., elastomers, and its computation and significance is described in detail in US Patent 5,449,560, for example.

[0046] To ensure that no further polymerization had continued in the polymer droplets of the emulsion, the polymer was extracted from the emulsion by the classical methanol/hexane breaking technique, and its viscosity was measured. It was found that the viscosity had remained the same as the viscosity of the neat polymer prior to emulsification. A gas chromatography (GC) analysis was conducted in order to determine the presence of any volatile cyclic silicone species which may have formed as a by-product during the procedure, i.e., such as the species octamethylcyclotetrasiloxane (D_4). The analysis showed only about 0.1 percent of D_4 .

Examples 2-4

[0047] Example 1 was repeated except that the amount of tin catalyst used in these three examples was 0.2 percent. The amount of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane used in these three examples also differed and this is shown below in Table 1. Examples 2 and 3 used an OH endblocked polydimethylsiloxane having a different degree of polymerization (DP), and this DP is shown in Table 1. Example 4, on the other hand, used a mixture containing 80 percent by weight of an OH endblocked polydimethyl siloxane having a degree of polymerization of about 560, and 20 percent by weight of an OH endblocked polydimethyl siloxane having a viscosity of about 90 mm²/s.

Table 1

	Example 2 Shorter PDMS DP 472	Example 3 Longer PDMS DP 945	Example 4 Blend of 2 PDMS (DP 560/DP 100)
Amount of Aminosilane	0.64 %	0.33 %	3 %
Time to Reach 100,000 mm ² /s	340 minutes	38 minutes	550 minutes
Tan Delta at 1 Hz	8.8	10.4	2.7

Examples 5-7

[0048] Example 1 was repeated using the same OH endblocked PDMS but using 0.52 percent by weight of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane. The result obtained by the phase inversion emulsification was a 100,000 mm²/s amine functional siloxane. These three examples also differed from Example 1 in the type of surfactant that was used in the emulsification, and this is shown below in Table 2. Elfan NS-242, it is noted, is an ethoxylated alkyl sulfate, obtained from Akzo Chemicals BV, Amersfoort, The Netherlands.

Table 2

	Example 5 Cationic Surfactant	Example 6 Nonionic Surfactant	Example 7 Anionic Surfactant
Name & Amount	ARQUAD 16-29 5 %	RENEX 30 4 %	ELFAN NS-242 4 %
Inversion Water Amount	0 %	4 %	15 %
Particle Size	1.5 μ m	0.4 μ m	1 μ m

Examples 8-10

[0049] Example 1 was repeated using the same materials. The tin catalyst was used in an amount of 0.2 percent by

weight. The amount of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane used in each of these three examples is shown below in Table 3. These examples show the effect of the silane amount on the crosslinking level (materialized by Tan Delta) of a 100,000 mm²/s copolymer.

Table 3

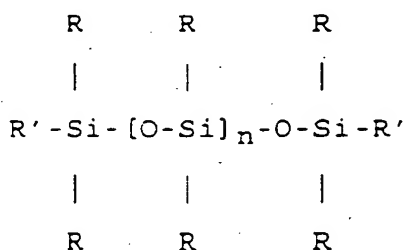
	Example 3 0.44 % of Aminosilane	Example 9 0.52 % of Aminosilane	Example 10 0.62 % of Aminosilane
Time to Reach 100,000 mm ² /s	450 minutes	134 minutes	82 minutes
Tan Delta at 1 Hz	11.8	9.9	3.7

Example 11

[0050] In this example, an amine functional siloxane gum, known to have been depolymerized, was used as a standard for purpose of comparison. It had a viscosity of about 85,000 mm²/s, and a tan delta at 1 Hz of about 10.7. An equivalent amine functional siloxane with a viscosity of 85,000 mm²/s, was prepared using the method according to this invention. It had a tan delta of about 13. This indicates that amine functional siloxanes prepared according to the present invention have a more plastic behavior, and are therefore less elastic. This is evidence that there exist a much lower number of branched monomers, and that the method according to the invention leads to the production of linear-like polymers.

Claims

1. A method of making a silicone oil-in-water emulsion containing a linear non-crosslinked silicone copolymer characterised in that the method comprises (A) polymerizing an OH endblocked polydiorganosiloxane with an amine functional trialkoxysilane in the presence of a metal catalyst; (B) adding to the reaction product of step (A) a carboxylic anhydride, and (C) subsequently emulsifying the copolymer prepared during polymerization step (A).
2. A method according to Claim 1 characterised in that the carboxylic anhydride is selected from the group consisting of acetic anhydride, benzoic anhydride, succinic anhydride, phthalic anhydride, and maleic anhydride.
3. A method according to Claim 1 or 2, characterised in that the OH endblocked polydiorganosiloxane comprises a substantially linear polymer of the structure:



wherein each R independently represents a hydrocarbon group having 1-20 carbon atoms or an aryl group; R' represents OH; and n is a positive integer greater than one.

4. A method according to any one of Claims 1 to 3 characterised in that the amine functional trialkoxysilane monomer is selected from the group consisting of 4-aminobutyltriethoxysilane; N-(2-aminoethyl)-3-aminopropyltrimethoxysilane; N-(6-aminohexyl)aminopropyltrimethoxysilane; 3-aminopropyltriethoxysilane; 3-aminopropyltrimethoxysilane; (3-aminopropyl)tris[2-(2-methoxyethoxy)ethoxy]silane; and 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane.
5. A method according to any of the preceding claims characterised in that the metal catalyst is selected from the

group consisting of stannous octoate, dimethyltin dilaurate, dibutyltin dilaurate, dibutyltin diacetate, dimethyltin dineodecanoate, dibutyltin dimethoxide, isobutyl tin tricerate, dimethyltin dibutyrate, dimethyltin dineodecanoate, triethyltin tartrate, tin oleate, tin naphthenate, tin butyrate, tin acetate, tin benzoate, tin sebacate, and tin succinate.

- 5 6. A method according to any of the preceding claims characterised in that the copolymer is emulsified using a nonionic surfactant.
- 10 7. A method according to any of the preceding claims characterised in that the copolymer is emulsified using a combination of a nonionic surfactant and a cationic surfactant.
8. A method according to any of Claims 1 to 6 characterised in that the copolymer is emulsified using a cationic surfactant.
- 15 9. A method according to any of Claims 1 to 6 characterised in that the copolymer is emulsified using an anionic surfactant.
- 20 10. A method according to any of the preceding claims characterised in that the silicone copolymer has a viscosity at 25°C in the range of from about 30,000 mm²/s to about 500,000 mm²/s, and in that the emulsion has an average particle size in the range of from about 0.3 µm to about 1.5 µm.
- 25 11. A method according to any of the preceding claims characterised in that less than about three percent by weight of amine functional trialkoxysilane is used based on the total weight of components used in the polymerization step A.
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(72) Inventors:

- **Dalle, Frederic**
06110 Le Canet (FR)
- **Marteaux, Leon**
1160 Bruxelles (BE)

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(74) Representative: **Vandamme, Luc Johan Roger**
Dow Corning Limited
Cardiff Road
Barry South Glamorgan CF6 7YL Wales (GB)

(71) Applicant: **DOW CORNING S.A.**
B-7180 Seneffe (BE)

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 9662

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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A,D	US 5 326 483 A (HALLORAN DANIEL J ET AL) 5 July 1994 (1994-07-05) * column 1, line 62 - column 2, line 54 *	1-10	
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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08G C08J
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 16 February 2001	Examiner Hoffmann, K
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 92 (PC/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-02-2001

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